COPPER DESORPTION IN A SOIL WITH VARIABLE CHARGE

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ABSTRACT: Adsorption processes of heavy metals in soils have been more extensively studied than desorption, in spite of this latter process being related to nutrient bioavailability in the soil solution. Copper desorption from surface (0-0.2 m) and subsurface (1.0 – 1.2 m) samples of an Anionic Acrudox was studied at two pH values (4.5 and 7.5). Soil samples were incubated with Cu rates varying from 0 to 400 mg kg^{-1}, during 4 and 12 weeks, in the presence of $CaCl_2$ as support electrolyte at concentrations of 0.01 and 0.001 mol L^{-1}. Complete soil adsorption of added Cu was observed at pH 7.5 in all incubation periods, indicating that a 24h-shaking period was enough to reach equilibrium and maximum adsorption. Copper adsorption varied with the incubation period and was much lower at pH 4.5 than at pH 7.5, after the 24 hour-incubation period. After 4 and 12 weeks, Cu adsorption values were higher and similar for all soil samples, irrespective of pH or depth of sampling. The effect of the incubation period on soil Cu adsorption surpassed the pH effect for all Cu rates. The hysteresis was expressive, suggesting that Cu enhances high-energy bonds with the soil colloids. Calcium chloride was not efficient in promoting native soil Cu desorption in the studied concentrations.
Key words: copper, desorption, ionic strength, pH

DESSORÇÃO DE COBRE EM SOLO COM CARGA VARIÁVEL

RESUMO: A adsorção de metais pesados aos solos é mais estudada do que sua dessorção. No entanto, o processo de dessorção está diretamente relacionado à disponibilidade dos elementos às plantas. A dessorção de cobre em amostras superficiais (0-0,2 m) e subsuperficiais (1,0-1,2 m) de um Latossolo Vermelho acriférrico foi estudada em dois valores de pH (4,5 e 7,5). Foram adicionados até 400 mg kg^{-1} de Cu em amostras incubadas por 4 e 12 semanas, tendo o $CaCl_2$ como eletrólito suporte nas concentrações de 0,01 e 0,001 mol L^{-1}. No pH mais elevado (7,5), em todos os períodos de incubação, as amostras adsorveram praticamente todo o cobre adicionado, indicando que o tempo de 24 h de agitação para se atingir o equilíbrio foi suficiente para atingir a adsorção máxima. A adsorção de Cu variou com o tempo de incubação do elemento com o solo. No pH mais baixo (4,5), a adsorção foi bem menor após 24 h de incubação. Após 4 e 12 semanas, as adsorções foram elevadas e semelhantes para todas as amostras, independentemente da profundidade e do pH. Para todas as doses estudadas, o efeito do tempo de incubação na adsorção de cobre pelo solo sobrepujou o efeito do pH. O fenômeno de histerese foi expressivo, sugerindo que o Cu forma ligações de alta energia com os colóides do solo. O cloreto de cálcio não foi eficiente para dessorver cobre nativo do solo.
Palavras-chave: cobre, dessorção, força iônica, pH

INTRODUCTION

The disposal of industrial residues and sewage sludges into Brazilian soils (Prado et at., 2002; Simonete & Kiehl, 2002; Martins et al., 2003; Pires & Mattiazzo, 2003) has been of considerable concern in recent years, mainly because of their possible high content in heavy metals, that may cumulate to toxic levels and constitute a potential hazard to plants, animals and mankind (Silveira et al., 1999; 2003). Adsorption-desorption reactions of metals at the soil colloidal surface affect their soil solution concentrations and, consequently, their availabilities to plants (Rodriguez-Rubio et al., 2003; Swift & McLaren, 1991). The metal retention by soils can be explained by three mechanisms: specific adsorption, ionic exchange and precipitation (Rodriguez-Rubio et al., 2003).

Organic matter and pH are the factors that directly or indirectly affect the Cu bioavailability (Rodriguez-Rubio et al., 2003; Yin et al., 2002). Organic radicals, as well as iron and aluminum oxides, have OH^- sites with high potential for specific Cu adsorption (Guilherme et

al., 1995; Silveira et al., 1999). In soils with pH lower than 2.5, Cu competes with protons for adsorption sites. However, at pH above 4.5, most charged sites are bound to Cu, due to the decreasing proton competition (Grimm et al., 1991). Between pH 4.0 to 6.0, Fe and Al oxides are the main cause of metal fixation and solubilization (Cavallaro & McBride, 1984). In relation to the soil native copper, Hogg et al. (1993) observed small desorption after a two-hour equilibrium, what evidenced low rate of Cu reaction with the soil colloids.

The objectives of this research were to evaluate the initial reaction time of Cu with an Anionic Acrudox soil during desorption process, the necessary shaking period for the native and added copper to reach equilibrium, the observation of the hysteresis phenomenon during the adsorption/desorption processes, and the desorption variation with the soil pH.

MATERIAL AND METHODS

Surface (0 and 0.2 m) and subsurface (1.0 and 1.2 m, in the highest expression of B-horizon) soil samples were collected from an Anionic Acrudox (LVwf), at the municipal district of Ribeirão Preto, State of São Paulo, Brazil (21º17'S, 47º81'W). Soil samples were sieved through a 2-mm screen, and two portions of 1.0 kg, air-dried soil were taken and thoroughly mixed with enough calcium carbonate ($CaCO_3$) or hydrochloric acid (HCl) to obtain pH values close to 4.5 and 7.5 and mimic soil conditions of acidity and alkalinity, respectively. These samples were incubated with 25% (m/m) of water, circa the soil's field capacity, at constant pH. Samples were their air-dried and sieved again through a 2-mm screen.

Chemical and physical analyses (Table 1) were performed according to Camargo et al. (1986): organic matter was oxidized with potassium dichromate to obtain organic carbon; pH was determined in 0.01 water using 1:2.5 (soil:solution) ratio; the zero point of salt effect (ZPSE) was obtained by titration with H^+ and OH^- in three concentrations of KCl, according to Alleoni & Camargo (1994); oxides concentrations were determined after sulfuric acid digestion; "free" iron was evaluated after dithionite reduction and sodium citrate reaction; poorly-crystallized iron and aluminum were dissolved in oxalic acid and their ammonium salts, and clay contents determined by the pipette method.

Native Cu adsorption and desorption

Soil samples previously incubated with either $CaCO_3$ or HCl were evaluated regarding native Cu desorption. The procedure to evaluate the ionic strength effect on Cu desorption was: 2 g of soil sample were transferred to 50-mL polyethylene tubes and 20 mL of 0.01 and 0.001 mol L^{-1} $CaCl_2$ solutions were added (Hogg et al., 1993; Zhu & Alva, 1993). The soil was mixed with the solution and the suspension was left steady during 24h to reach equilibrium, as recommended by Gupta & Mackay (1966). The suspension was shaken for either 2, 4 or 8 hours to evaluate Cu desorption. Since no effect of the shaking period was observed (data not shown), the period of 2 h was chosen. At least ten desorption procedures per each sample were done, as follows: after each 2-h period, the soil:solution suspension was centrifuged at 4,000 rpm, and the supernatant was filtered through blue ribbon paper filter and collected for subsequent Cu determination. The soil in the tube was resuspended in new electrolyte solution. All procedure for the desorbed Cu determination was then repeated for ten consecutive times. The Cu contents in the collected supernatant solutions were determined by atomic absorption spectrometry, and the accumulated quantity of desorbed Cu was calculated by adding up the Cu contents in each equilibrium solution. All determinations were made in duplicates.

Native Cu extracted with DTPA

The native copper was also extracted with a 0.005 mol L^{-1} DTPA solution, following routine extracting procedure for the determination of available Cu for fertilizer recommendation purposes (Raij et al., 2001). All determinations were made in duplicates, and compared to the accumulated quantities of native Cu determined by the desorption procedure described above.

Adsorption and desorption of added Cu

The added Cu desorption, by adding $CuCl_2$, was proceeded in soil samples with two pH values (4.5 and 7.5) and evaluated during three periods of soil/Cu incubation for either 24 hours, according to Gupta & Mackay (1966), 4 or 12 weeks (Hogg et al., 1993), with moisture content kept at 25% (soil field capacity). Hogg et al. (1993), studying Cu adsorption in ten soils from New Zealand, concluded that a period of incubation of 12 weeks was adequate, because adsorption was very low afterwards.

Table 1 - Chemical and physical characteristics of the Anionic Acrudox.

Depth	C	pH H_2O	ΔpH	ZPSE	SSA	Ki	Fe_2O_3 Total	Fed	Fe_{ox}	Al_2O_3 Total	Al_{ox}	Clay
m	g kg^{-1}				m^2 g^{-1}		---------- g kg^{-1} ----------					
0 - 0.2	20.0	6.4	-0.9	3.3	38	0.93	320	160	13	200	10	60
1.0 - 1.2	5.0	5.3	0.3	6.3	24	0.87	240	170	9	200	7	64

ZPSE = Zero point of salt effect; SSA = specific surface area; Fed = "free" iron; Fe_{ox} = poorly-crystallized; Al_{ox} = "free" aluminum

The quantities of Cu added to the soil for adsorption and 24 hours later for desorption were 5, 20, 50, 100, 200, 400, and 600 mg kg^{-1}. Treatments correspondent to the 4 and 12-week incubation periods received the intermediary rates of 20, 100 and 400 mg kg^{-1}. The soil Cu adsorption was evaluated after shaking during 24 hours, by subtracting the Cu determined in the equilibrium solution from the Cu initially added. After the 24h-shaking period, at least ten 2h-periods of desorption were evaluated for each sample, using 0.01 and 0.001 mol L^{-1} $CaCl_2$ solutions, following the same procedure described for the native Cu desorption determination. After centrifugation and separation of the supernatant solution, the soil was resuspended in new electrolyte solution, restarting the procedure of Cu desorption determination, which was repeated ten times. The equilibrium solutions collected were analyzed for Cu by atomic absorption spectrometry. All determinations were run in duplicates.

RESULTS AND DISCUSSION

Cu adsorption

The Anionic Acrudox studied is rich in iron and aluminum oxides (Table 1). The oxides as well as the organic matter define the magnitude of the specific Cu adsorption (Silveira et al., 2002; Silveira & Alleoni, 2003; Rodriguez-Rubio et al., 2003) and thus, the specific Cu adsorption is little affected by the ionic strength variation (Zelazny et al., 1996). Such considerations indicate that Cu is adsorbed as an inner-sphere complex and does not participate of the soil exchange complex. The ZPSE in the soil surface layer was 3.3, with negative charge balance in both studied pH values, whereas in depth, the ZPSE was 6.3, with positive charge balance at the lower pH value (4.5).

Oxisols with acric properties have effective cation exchange capacity (ECEC) lower than 15 $mmol_c$ kg^{-1} of clay and the pH of B-horizon pH measured in 1.0 mol L^{-1} KCl, higher than or equal to 5.0, in a 1.5 m depth (Soil Survey Staff, 1990). Such soils are common in tropical regions and predominate over a wide area in the North of the State of São Paulo, Brazil, where they are intensively cultivated. In the Anionic Acrudox B-horizon, the difference between the zero point of charge (ZPC) and pH is small. In many cases, the ZPC value surpasses the pH value, giving rise to a positive charge balance to the soil, that becomes predominantly an anion exchanger. This charge reversion phenomenon almost always occurs in soil depths greater than 0.5 m, because in such situation the organic matter, in which ZPC is very low ($\cong$ 2.0), practically has no effective action (Uehara, 1988). As a matter of fact, Silveira & Alleoni (2003), studying an Anionic Acrudox, observed that surface horizon adsorbed higher Cu amounts than the subsurface horizon, thus evidencing the influence of soil organic matter upon this metal adsorption.

Copper adsorption varied with the soil incubation period. At higher pH values (7.5), in all incubation periods, adsorption was similar for both samples and corresponded practically to all added Cu (Figures 1 and 2). The 24h-shaking period to reach equilibrium was thus enough to attain the maximum adsorption. Rodriguez-Rubio et al. (2003), also found significant Cu adsorption in Spanish soils with pH 7.8, using 24h-shaking period to reach equilibrium. The high Cu adsorption at higher pH was similar to that observed by Ponizovsky et al. (2001) in a Chernozen under forest and a Podzol, both in Russian territory. At lower pH (4.5), Cu adsorption was lower only after 24 h-incubation; however, past 4 and 12 weeks, both soil samples showed similar Cu adsorption values, irrespective of sampling depth or pH.

Considering that the Anionic Acrudox (LVwf) shows variation in charge balance as pH changes, presenting more positive charges with increasing external acidity, the decreased amount of negative charges at lower pH values was seemingly not enough to adsorb all Cu during the 24-hour-incubation period. Nevertheless, the Cu-adsorption evolved to higher values after 4- and 12-week-incubation. Such slow Cu adsorption reaction with soil colloids has already been noticed by Barrow (1985) and Hogg et al. (1993), especially for organic colloids.

In the range of the Cu application rates, the incubation period effect on soil Cu-adsorption surpassed the pH effect. Although the difference observed between the surface and subsurface layers ZPSE values (3.3 and 6.3, respectively) (Table 1), the latter with a positive balance of charge at pH 4.5, the soil Cu-adsorption values were not different when soil samples were incubated for 4 and 12 weeks (Figure 1). Thereafter, the contact period between Cu and soil must be taken into account in adsorption studies of this metal by soil colloids, as previously appointed by Nascimento et at. (2003) for soils fertilized with Cu.

Desorption of native Cu

The amount of DTPA-extracted Cu decreased as soil pH increased, as already observed by Camargo et al. (1982) in 24 surface soil samples of the State of São Paulo, Brazil. As a matter of fact, DTPA had been described as an efficient soil Cu extracting solution for the purpose of fertilization recommendations for several crops (Abreu et al., 1996). Calcium chloride was inefficient to evaluate native Cu desorption by the Anionic Acrudox in the used concentrations. In spite of not showing selectivity in relation to calcium, Cu seems to be more tightly bound to the soil than by a simple ionic exchange.

The procedures of desorption extracted very little native soil Cu at both pH values, irrespective of shacking periods and $CaCl_2$ concentrations. Hogg et al. (1993), using 0.01 mol L^{-1} $Ca(NO_3)_2$ solution, also extracted small cumulative quantities of native copper desorbed of ten

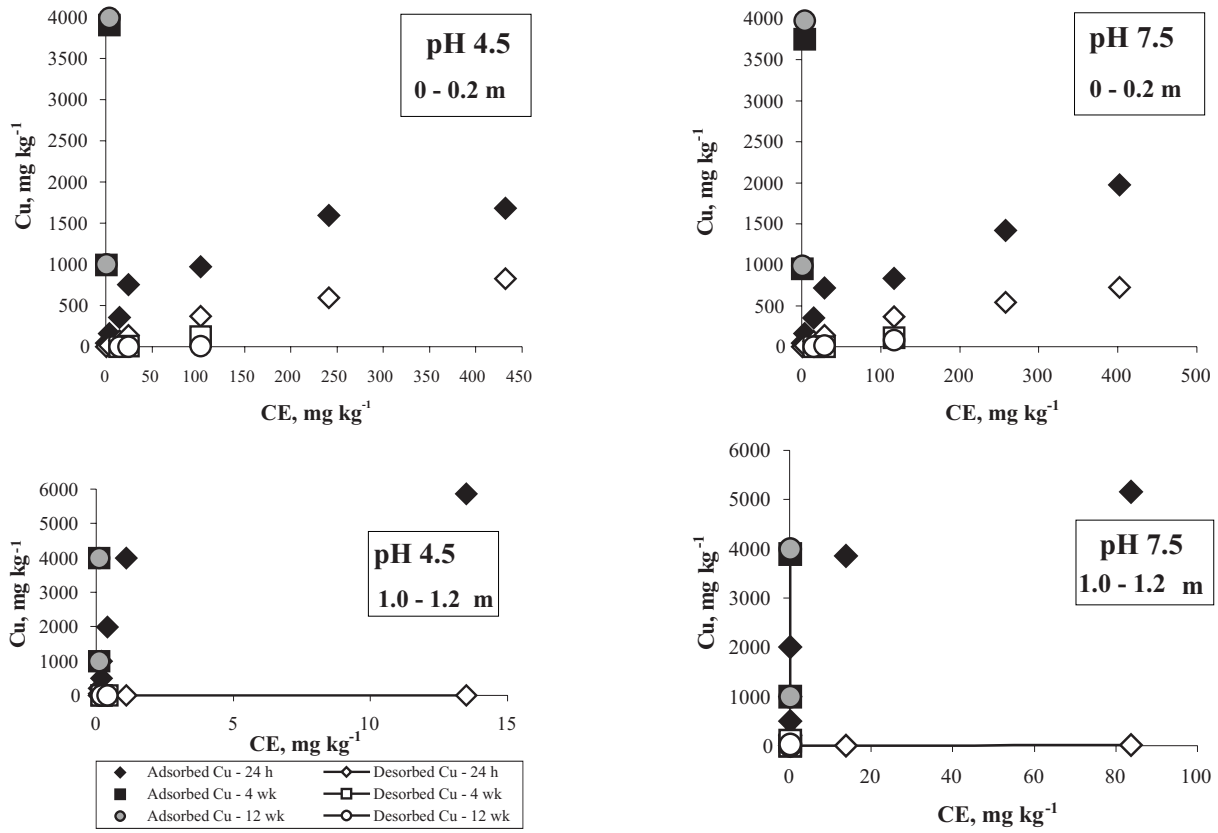

Figure 1 - Adsorption and desorption of Cu added to surface and subsurface samples, of an Anionic Acrudox incubated during 24 hours, 4 and 12 weeks, at pH 4.5 and 7.5, using 0.01 mol L^{-1} $CaCl_2$ solution (CE = concentration in the equilibrium solution).

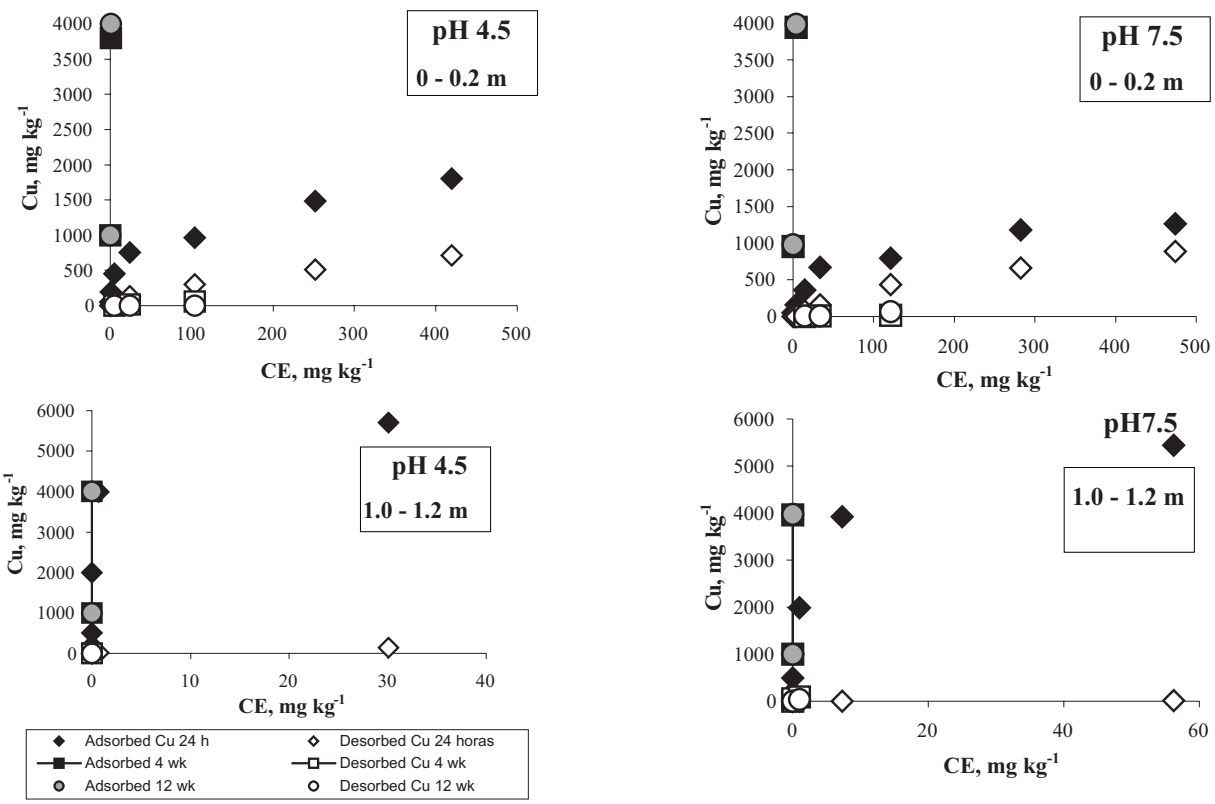

Figure 2 - Adsorption and desorption of Cu added to soil samples collected from the surface and in depth, and incubated during 24 hours, 4 and 12 weeks, with pH 4.5 and 7.5, using 0.001 mol L^{-1} $CaCl_2$ solution (CE = concentration in the equilibrium solution).

soils from New Zealand, with a variation of 0.087 to 0.171 mg kg^{-1}. DTPA extracted large amounts of available copper in the surface layers, mainly at low pH values, and under limits set by Raij et al. (1997). For the studied pH values, the quantities of extracted copper ranged from 7.3 to 4.6 mg kg^{-1} in the surface, and from 1.5 to 0.3 mg kg^{-1} in the subsurface samples (Table 2).

Desorption of added Cu

Each soil sample was desorbed at least ten times, and the desorption procedure was interrupted when desorbed Cu quantities were lower than 0.01 mg kg^{-1} of soil.

Table 2 - Variation in the Cu contents in the desorption solution and DTPA-extracting solution, with pH values, in soil samples from an Anionic Acrudox.

Depth	pH	Desorbed Cu	DTPA- Cu
m		---------- mg kg^{-1} ----------	
0-0.2	4.8	0.1	7.3
	6.6	0.01	6.1
	6.9	0	4.6
	7.7	0	4.7
1.0-1.2	4.2	0.01	1.5
	5.5	0	1.4
	6.9	0	1.2
	7.7	0	0.3

It was recorded copper desorption of 17 % in the surface- and of 23 % in the subsurface-soil samples, in both support electrolyte concentrations, for the added Cu rate of 100 mg kg^{-1} at pH 4.5 and without incubation, whereas at pH 7.5, desorption was practically null. The quantity of desorbed copper increased as pH decreased, since the number of positive charges increased, as was already noticed by Temminghoff et al. (1994) and Wang et al. (2003). At low pH, Cu might be adsorbed in the exchangeable form, while at higher pH, specific adsorption might occur (Wang et al., 2003). For soil incubation periods of 4 and 12 weeks, desorption values were very low, reaching up to 0.l to 0.3 % of the total absorbed Cu, respectively. When pH values were higher, in all incubation periods, desorption was practically null (Figures 1, 2 and 3).

Cumulative desorption evidences strong interaction between Cu and soil colloids, and the period of contact plays an important role (Figure 3). The largest desorbed quantity occurred after a 24h incubation, and the smallest after a 12-week period. These results are similar to those reported for Cu desorption by goethite (Padmanabham, 1983a, b) and by soils (Lehmann & Harter, 1984). In both papers, the longer the period between the initial adsorption and desorption, the higher the quantity of copper irreversibly adsorbed. The slow Cu adsorption reactions into the soil are responsible for the re-

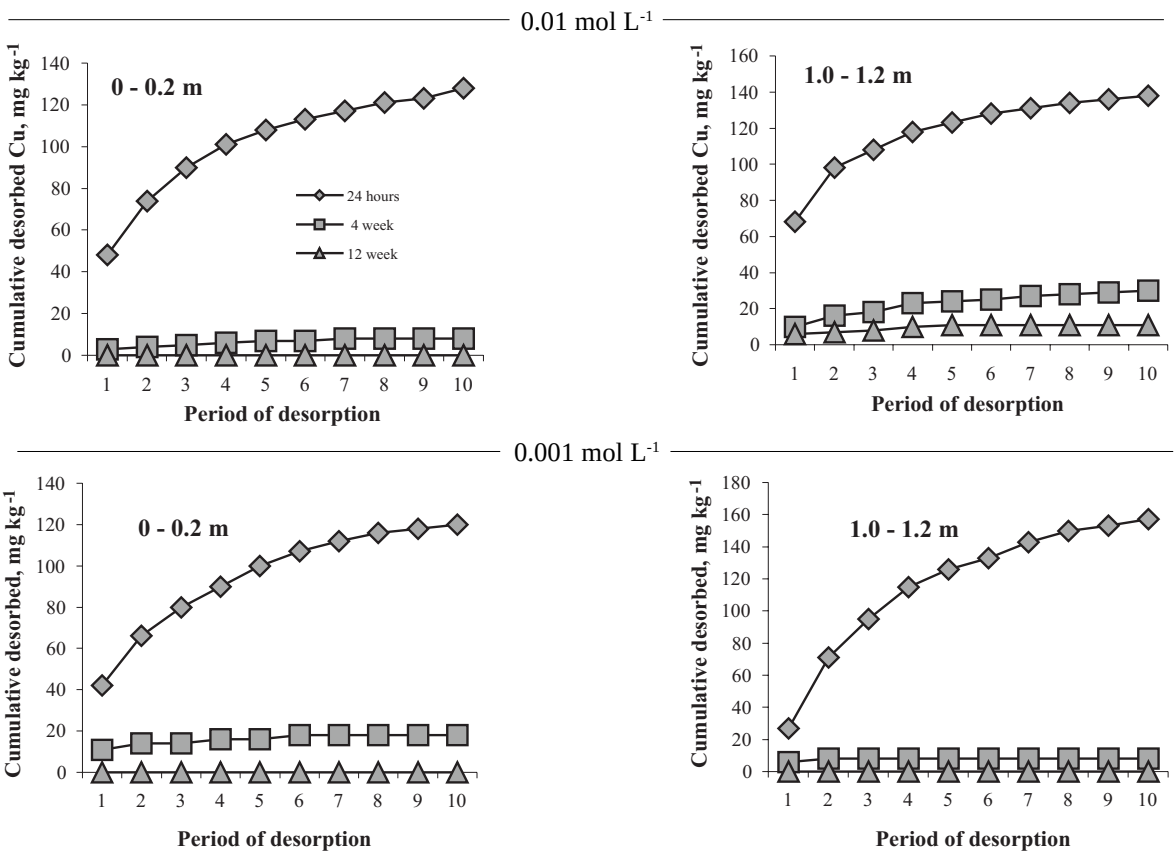

Figure 3 - Cumulative desorption of added Cu (100 mg dm^{-3}), incubated surface and subsurface soil samples of an Anionic Acrudox, during 24 hours, 4 and 12 weeks, for pH 4.5, using 0.01 and 0.001 mol L^{-1} $CaCl_2$ solutions.

duced possibility of desorption of this element to the soil solution (McLaren et al., 1983 and Hogg et al., 1993) with subsequent implications regarding its availability to plants in long terms (Hogg et al., 1993).

The hysteresis phenomenon was expressive, as already observed by Padmanabham (1983a, b) and Wu et al. (1999), suggesting that Cu makes high-energy bonds with soil colloids. The first author considered the presence of two adsorption sites in the goethite surface, one of fast and the other of slow desorbing fraction; the other authors suggested that specific adsorption predominantly occurred by soil colloids.

As general conclusions, pH affected Cu adsorption and desorption only at time zero (24 h) of incubation. After 4 and 12 weeks of incubation, adsorption was about the same for the tested pH values. Calcium chloride was inefficient in desorbing native soil copper.

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